



Selective Isomerization of Electron Deficient Vinylcyclopropanes by Thermal Action of Pentacarbonyl Iron

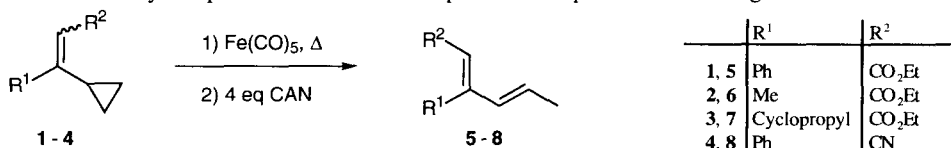
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Abstract: The response of a variety of vinylcyclopropanes, bearing an ester group in the β -position, upon exposure to pentacarbonyl iron at elevated temperatures is established. Dienic esters with a single configuration of the double bonds are obtained by this route in high yield. Steric and electronic factors, governing the course of the reactions, were investigated using nitrile and alkyl substituted vinylcyclopropanes.

The exploitation of transition metal assisted reactions of various vinylcyclopropanes is regarded as an area of current interest in organic chemistry.¹ Among the utilized metals are nickel,² palladium,³ rhodium,⁴ chromium⁵ and iron.⁶ Despite several early reports, a few decades ago, dealing with pentacarbonyl iron mediated transformations of vinylcyclopropanes, little attention has been paid to the influence of common functional groups in the outcome of such events.⁷ Our efforts, aimed towards synthetic application, revealed a distinct behavior of electron deficient vinylcyclopropanes upon exposure to pentacarbonyl iron at elevated temperatures.

Our isomerization protocol required treatment of the esters **1** - **3** with $\text{Fe}(\text{CO})_5$ (2.0 equiv.) under an inert atmosphere at 150°C overnight.⁸ Liberation of the ligand was accomplished by stirring the crude product, in anhydrous THF, in the presence of ceric ammonium nitrate (CAN) for 2 h at ambient temperature. Extraction with ether and evaporation of the solvent *in vacuo* gave a residue, which was purified by chromatography. Every experiment carried out by this procedure exhibited complete consumption of the starting material.

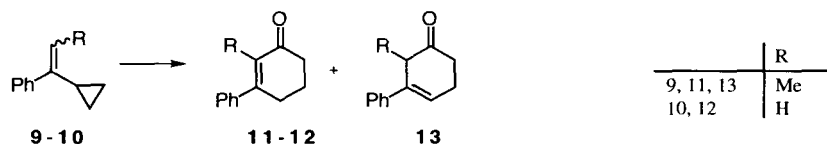


Dienes **5** and **6** were obtained pure in yields of 85 and 92% respectively.⁹ A somewhat lower degree of efficiency was observed with **7**, acquired in 75% yield. The illustrated configuration of the generated double bonds was a common feature of **5** - **7** as determined by NOE studies and examination of the appropriate coupling constants.^{10,11}

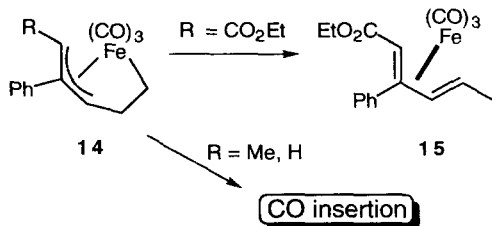
Production of dienes from vinylcyclopropanes using this method depends heavily on the substituents and thus the electronic properties of the double bond. Employing a vinylcyclopropane with a different electron withdrawing group, such as the nitrile **4**, did not alter the course of the reaction and produced the diene **8** in an analogous manner to the esters **5** - **7**.¹²

Replacing the ester and nitrile group with an alkyl moiety altered the course of the reaction entirely. We treated a wide variety of vinylcyclopropanes with $\text{Fe}(\text{CO})_5/\text{CAN}$ and discovered a striking selection of pathways.¹³ Although the hydrocarbon **9** reacted much more slowly than **1** - **4** under the applied conditions, the ketones **11** and **13** were the only products, besides unreacted **9**.¹⁴

Omitting any substitution at C-2 enhanced the reactivity of vinylcyclopropanes towards carbon monoxide insertion dramatically. Hence treatment of **10** with $\text{Fe}(\text{CO})_5/\text{CAN}$ supplied **12** almost quantitatively.¹⁵



On the basis of these results, and previous studies concerning the reaction of $\text{Fe}(\text{CO})_5$ with vinylcyclopropanes, we suggest the following mechanistic rational.¹⁶ Coordination of an unsaturated iron carbonyl species to the double bond and subsequent ring opening generate **14** ($\text{R} = \text{CO}_2\text{Et}$). At this stage, the electronic scenery appears to be decisive for the succeeding pathway. Our findings demonstrate that two competitive routes must exist, arising from **14**.



In general, σ, π -allylic intermediates like **14** are prone to yield π -diene complexes at elevated temperatures.¹⁷ Considering this particular case, the anticipated process would occur with a remarkable stereoselectivity giving the intended iron complex **15**. Subsequent oxidative removal of the metal should not interfere with the final stereochemistry of the organic substrate.

In order to collect further evidence for a plausible mechanistic rational of these reaction pathways, we are trying now to isolate and characterize potential intermediates. Additionally, possible applications of the above mentioned reactive species are currently being elaborated in this laboratory and will be reported in due course.

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References and Notes

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2. a) Ryu, I.; Ikura, K.; Tamura, Y.; Maenaka, J.; Ogawa, A.; Sonoda, N. *Synlett* **1994**, 941. b) von Doering, W.; Roth, W. R. *Tetrahedron*, **1963**, 19, 715.
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4. Jun, C.-H.; Kang, J.-B.; Lim, Y.-G. *Tetrahedron Lett.* **1995**, 36, 277.
5. Salzer, A. *J. Organomet. Chem.* **1976**, 117, 245.
6. Aumann, R. *Angew. Chem.* **1973**, 85, 628; *Angew. Chem. Int. Ed. Engl.* **1973**, 12, 574.
7. Review : Sarel, S. *Acc. Chem. Res.* **1978**, 11, 204.
8. Lower temperature and less $\text{Fe}(\text{CO})_5$ (e. g. 110°C and 1.2 equiv.) are also suitable, but we selected this uniform procedure for reasons of comparison, diglyme is a preferable solvent.
9. Purity is within experimental detection limits.
10. A previous report stated the isomerization of the unsubstituted vinylcyclopropane to isomeric 1,3-pentadienes under similar conditions, see : Aumann, R. *J. Am. Chem. Soc.* **1974**, 96, 2631.
11. Selected spectral data for **1** - **3**: **1**: ^1H -NMR (400 MHz, CDCl_3) δ = 1.05 (t, J = 7 Hz; 3 H), 1.78 (dd, J = 7 and 1.5 Hz; 3 H), 3.97 (q, J = 7 Hz; 2 H), 5.57 (dq, J = 15 and 7 Hz; 1 H), 5.85 (s, 1 H), 6.35 (dd, J = 16 and 1 Hz; 1 H), 7.11 - 7.39 (m, 5 H). **2**: ^1H -NMR (250 MHz, CDCl_3) δ = 1.27 (t, J = 7 Hz; 3 H), 1.84 (d, J = 5 Hz; 3 H), 2.25 (d, J = 1 Hz; 3 H), 4.15 (q, J = 7 Hz; 2 H), 5.66 (s, 1 H), 6.11 (m, 2 H). **3**: ^1H -NMR (400 MHz, CDCl_3) δ = 0.58, 0.77 (2m, 4 H), 1.19 (t, J = 7 Hz; 3 H), 1.66 (dd, J = 7 and 1 Hz; 3 H), 2.83 (m, 1 H), 4.07 (q, J = 7 Hz; 2 H), 5.54 (d, J = 15 Hz; 1 H), 5.77 (s, 1 H), 6.05 (m, 1 H).
12. Selected spectral data for **4**: ^1H -NMR (400 MHz, CDCl_3) δ = 1.78 (d, J = 7 Hz; 3 H), 5.27 (s, 1 H), 5.78 (dq, J = 16 and 7 Hz; 1 H), 6.30 (d, J = 16 Hz; 1 H), 7.18 - 7.40 (m, 5 H).
13. Unpublished results from this laboratory.
14. Ratio of products : 22% **9**, 12% **11** and 18% **13**.
15. The reaction of **10** under identical conditions is reported to give the corresponding diene complex and no CO insertion. Our findings contradict this result. Repeated experiments confirmed the trend of exclusive CO insertion with **10**. Leading reference : Sarel, S.; Ben-Shoshan, R.; Kirson, B. *J. Am. Chem. Soc.* **1965**, 87, 2517.
16. This proposed mechanism is based on a study with the parent compound vinylcyclopropane, see reference 12.
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